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# MULTICOMPONENT SYSTEM FOR MODIFICATION, DECOMPOSITION OR BLEACHING OF LIGNIN, LIGNIN-CONTAINING MATERIALS OR SIMILAR SUBTANCES, AND METHOD FOR USING IT

Inventor: Dr. Hans-Peter Call
52551 Übach-Palenberg, DE

Applicant: Consortium for the Electrochemical Industry GmbH
81379 Munich, DE

Agent: Dr. E. Franke
81737 Munich

[Abstract]

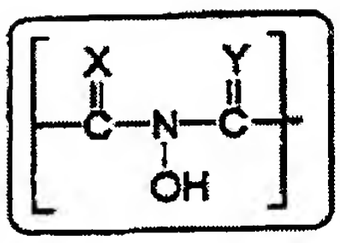
A multicomponent system for modification, decomposition or bleaching of lignin, lignin-containing materials, or similar substances, containing

a. optionally at least one oxidation catalyst and

b. at least one suitable oxidation agent and

c. at least one mediator,

which is characterized by the fact that the mediator is chosen from the group of cyclic N-hydroxy compounds with at least one, optionally substituted, five- or six-member ring containing the structure indicated in formula A



Formula A

and its salts, ethers or esters, where

X and Y are the same or different, and mean O, S or $NR^1$, where

$R^1$ means hydrogen, hydroxy, formyl, carbamoyl, sulfono residue, ester or salt of the sulfono residue, sulfamoyl, nitro, amino, phenyl, aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl, phospho, phosphono, phosphonooxy residue, esters or salts of the phosphonooxy residue, where carbamoyl, sulfamoyl, amino and phenyl residues can be unsubstituted or substituted one or more times with a residue $R^2$, and the aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl residues can be saturated or unsaturated, branched or unbranched, and can be substituted one or more times with a residue $R^2$, where,

$R^2$ is the same or different and means hydroxy, formyl, carboxy, ester or salt of the carboxy residue, carbamoyl, sulfono ester or salt …

Description

This invention concerns a multicomponent system for modification, decomposition or bleaching of lignin, lignin-containing materials, or similar substances, and a method for its use. One may mention the sulfate and the sulfite processes as the methods that are mainly used today for pulp manufacture. With both methods pulp is produced by cooking under pressure. The sulfate process operates with the addition of NaOH and $Na_2S$, while $Ca(HSO_3)_2 + SO_2$ are used in the sulfite process.

All of the methods have as the primary goal the removal of the lignin from the plant material that is used, wood or annual plants.

The lignin, which together with the cellulose and hemicellulose makes up the primary component of the plant material (stalk or trunk) must be removed, since otherwise it is not possible to produce nonyellowing and mechanically durable papers.

The pulp production process operates with grindstones (wood pulp) or with refiners (TMP), which defiberize the wood by beating after the appropriate pretreatment (chemical, thermal or chemical-thermal).

These pulps still contain a large proportion of the lignin. They are used primarily for the production of newsprint, illustration print, etc.

For some years there has been research carried out into the possibilities of using enzymes for lignin decomposition. The mechanism of action of such lignolytic systems was first explained

only a few years ago, when it became possible to obtain sufficient amounts of enzyme through appropriate cultivation conditions and addition of inductors with the white rot fungus *Phanerochaete chrysosporium*. In doing so, the previously unknown lignin peroxidases and manganese peroxidases were discovered. Since *Phanerochaete chrysosporium* is a very efficient lignin decomposition agent, there were attempts to isolate its enzymes and to use them in purified form for lignin decomposition. However, this was not successful, since it turned out that the enzymes primarily lead to repolymerization of the lignin and not to its decomposition.

The situation is also similar for other lignolytic enzyme species like laccases, which oxidatively decompose lignin with the aid of oxygen instead of hydrogen peroxide. It was found that similar processes occur in all instances. Specifically, radicals that again react with themselves and thus lead to polymerization are formed.

Thus, today there are only processes that operate with in vivo systems (fungus systems). The main bottlenecks in optimization attempts are the so-called biopulping and biobleaching.

Biopulping is understood to be the treatment of wood chip with living fungus systems.

There are 2 forms:

1. Pretreatment of wood chip before refining or grinding in order to save energy in the production of pulp (for example, TMP or wood pulp).

Another advantage is the improvement of the mechanical properties of the pulp that occurs most often, while a disadvantage is the poorer end whiteness.

2. Pretreatment of wood chip (softwood/hardwood) before the pulp digester (Kraft process, sulfite process).

Here the goal is to reduce the quantity of cooking chemicals, to improve the cooking capacity, and "extended cooking."

Also, an advantage is improved kappa number reduction after cooking compared to cooking without pretreatment is achieved.

Disadvantages of this method are without question the long treatment times (several weeks) and, above all, the unsolved danger of contamination during treatment, if one wishes to omit the sterilization of the wood chip, which is probably uneconomical.

Biobleaching also operates with in vivo systems. The cooked pulp (softwood/hardwood) is inoculated with fungus before bleaching and treated for days to weeks. Only after this lengthy treatment time does one see a significant reduction of the kappa number and improvement of whiteness, which makes the process uneconomical for implementation in the current bleaching sequences.

Another application that is carried out mostly with immobilized fungus systems is the treatment of the pulp fabrication wastewaters, in particular bleaching wastewaters, to decolorize

them and reduce their AOX (reduction of chlorinated compounds in the wastewater that give rise to chlorine and chloride dioxide bleaches).

Moreover, the use of hemicellulases, including xylanases and mannases, as "bleach boosters."

These enzymes are intended mainly to counteract the xylan that is reprecipitated after the cooking process and that in some cases covers up the residual lignin and through its decomposition to increase the accessibility of the lignin for the bleaching chemicals (mainly chlorine dioxide) that are used in the subsequent bleaching sequences. The savings of bleaching chemicals seen in the laboratory was only conditionally confirmed on an industrial scale, so that at best this type of enzyme can be categorized as a bleach additive.

Besides the lignolytic enzymes, chelate substances (siderophores like ammonium oxalate) and biosurfactants are accepted as cofactors.

A system for removal of lignin from lignin cellulose-containing material with simultaneous bleaching that operates with lignolytic enzymes from white rot fungi with the addition of reduction and oxidation agents and phenolic compounds as mediators is described in PCT/EP87/00635.

In DE 40 08 893 C2 "mimic substances," which simulate the active center (prosthetic group) of lignolytic enzymes, are added to redox systems. In this way a considerable improvement of performance was achieved.

In PCT/EP92/01086 a redox cascade with the aid of phenolic or nonphenolic substances that are "matched" in oxidation potential are used as additional improvement.

With all three methods the limitation for large-scale use is the usability at low stock consistencies (to a maximum of 4%) and, in the case of the last two applications, the danger of leaching out of metals when using the chelate compounds, which can lead to decomposition of the peroxide, above all when there are connected peroxide bleaching steps.

Methods in which the activity of peroxidase is promoted with so-called enhancer substances are known from WO/12619, WO 94/12620 and WO 94/12621.

The enhancer substances are characterized in WO 94/12619 by means of their half-lives.

In accordance with WO 94/12620 enhancer substances are characterized by the formula A = N – N = B, where A and B each are defined cyclic residues.

According to WO 94/12620, enhancer substances are organic chemicals that contain at least two aromatic rings, of which at least one is substituted with specifically defined residues.

All three applications concern "dye transfer inhibition" and the use of the relevant enhancer substances together with peroxidases as detergent additive or detergent composition in laundry detergents. Applicability to the treatment of lignin is indeed mentioned in the description of the application, but special tests with the substances specifically disclosed in the applications

showed that they have no effect as mediators for increasing the bleaching action of peroxidases in the treatment of lignin-containing materials!

WO 94/29510 describes a method for enzymic delignification, in which enzymes are used together with mediators. Generally, compounds with the structure NO-, NOH- or HRNOH are disclosed as mediators.

Of the mediators disclosed in WO 94/29510, 1-hydroxy-1H-benzotriazole (HBT) offers the best results in delignification. However, HBT has various disadvantages: it is available only at high cost and in amounts that are not sufficient.

Under delignification conditions it reacts to form 1H-benzotriazole. This compound is poorly degradable and thus in larger amounts represents a considerable environmental burden.

Moreover, 1-hydroxy-1H-benzotriazole reacts under the effect of oxidation agents such as are used in delignification and forms other degradation products, which have not been more precisely characterized, and which have an undesirable strong color.

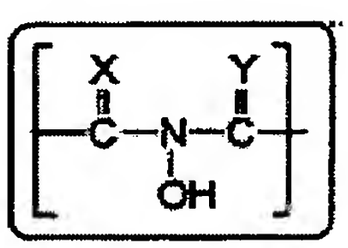
This invention concerns a multicomponent system for modification, decomposition or bleaching of lignin, lignin-containing materials, or similar substances, containing

a. optionally at least one oxidation catalyst and

b. at least one suitable oxidation agent and

c. at least one mediator,

which is characterized by the fact that the mediator is chosen from the group of cyclic N-hydroxy compounds with at least one, optionally substituted, five- or six-member ring containing the structure indicated in formula A




Formula A

and its salts, ethers or esters, where

X and Y are the same or different, and mean O, S or $NR^1$, where

$R^1$ means hydrogen, hydroxy, formyl, carbamoyl, sulfono residue, ester or salt of the sulfono residue, sulfamoyl, nitro, amino, phenyl, aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl, phospho, phosphono, phosphonooxy residue, esters or salts of the phosphonooxy residue, where carbamoyl, sulfamoyl, amino and phenyl residues can be unsubstituted or substituted one or more times with a residue $R^2$, and the aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl residues can be saturated or

unsaturated, branched or unbranched, and can be substituted one or more times with a residue $R^2$, where,

$R^2$ is the same or different and means hydroxy, formyl, carboxy, ester or salt of the carboxy residue, carbamoyl, sulfono ester or salt of the sulfono residue, sulfamoyl, nitro, amino, phenyl, $C_1$-$C_5$ alkyl, $C_1$-$C_5$ alkoxy residue.

The multicomponent system in accordance with the invention contains mediators that are available industrially and are cheaper than HBT. These mediators react under the effect of oxidation agents to form products without troublesome coloration. These products are in turn completely degradable.

Preferably the multicomponent system in accordance with the invention includes at least one oxidation catalyst.

Enzymes are preferably used as oxidation catalysts in the multicomponent system in accordance with the invention. In the sense of the invention the term enzyme also includes enzymically active proteins or peptides or prosthetic groups of enzymes.

Oxidoreductases of classes 1.1.1 through 1.97 in accordance with the International Enzyme Nomenclature, Committee of the International Union of Biochemistry and Molecular Biology (Enzyme Nomenclature, Academic Press, Inc., 1992, pp. 24-154) can be used as enzyme in the multicomponent system in accordance with the invention.

Preferably, enzymes of the following classes are used:

Enzymes of class 1.1, which includes all dehydrogenases that act on primary, secondary alcohols and semiacetals, and that have as acceptors $NAD^+$ or $NADP^+$ (subclass 1.1.1), cytochrome (1.1.2), oxygen ($O_2$) (1.1.3), disulfides (1.1.4), quinones (1.1.5), or other acceptors (1.1.99).

Of this class the enzymes of class 1.1.5 with quinones as acceptors and enzymes of class 1.1.3 with oxygen as acceptor are especially preferred.

Especially preferred in this class is cellobiose:quinone-1-oxidoreductase (1.1.5.1).

Additionally preferred are enzymes of class 1.2. This enzyme class (1.1.5.1) includes enzymes that oxidize aldehydes to the corresponding acids or oxo groups. The acceptors can be $NAD^+$, $NADP^+$ (1.2.1), cytochrome (1.2.2), oxygen (1.2.3), sulfides (1.2.4), iron-sulfur proteins (1.2.5) or other acceptors (1.2.99).

Especially preferred here are the enzymes of the group (1.2.3) with oxygen as acceptor.

Additionally preferred are enzymes of class 1.3. This class includes enzymes that act on CH-CH groups of the donor.

The corresponding acceptors are $NAD^+$, $NADP^+$ (1.3.1), cytochrome (1.3.2), oxygen (1.3.3), quinone or related compounds (1.3.5), iron-sulfur proteins (1.3.7) or other acceptors (1.3.99).

Especially preferred is bilirubin oxidase (1.3.3.5).

Here the enzymes of class (1.3.3) with oxygen as acceptor (1.3.5) and with quinone, etc. as acceptor are especially preferred.

Additionally preferred are enzymes of class 1.4, which act on CH-$NH_2$ groups of the donor.

The corresponding acceptors are $NAD^+$, $NADP^+$ (1.4.1), cytochromie (1.4.2), oxygen (1.4.3), disulfides (1.4.4), iron-sulfur proteins (1.4.7) or other acceptors (1.4.99).

Especially preferred here are also the enzymes of class 1.4.3 with oxygen as acceptor.

Additionally preferred are enzymes of class 1.5, which act on CH-NH groups of the donor. The corresponding acceptors are $NAD^+$, $NADP^+$ (1.5.1), oxygen (1.5.3), disulfide (1.5.4), quinone (1.5.5) or other acceptors (1.5.99).

Here, too, enzymes with oxygen ($O_2$) (1.5.3) and with quinones (1.5.5) as acceptors are especially preferred.

Additionally preferred are enzymes of class 1.6, which act on NADH or NADPH.

The acceptors here are $NADP^+$ (1.6.1), heme proteins (1.6.2), disulfide (1.6.4), quinone (1.6.5), $NO_2$ groups (1.6.6) and a flavin (1.6.8) or certain other acceptors (1.6.99).

Especially preferred here are enzymes of class 1.6.5 with quinones as acceptors.

Additionally preferred are enzymes of class 1.7, which act on other $NO_2$ compounds as donors and have, as acceptors, cytochrome (1.7.2), oxygen ($O_2$) (1.7.3), iron-sulfur proteins (1.7.7) or others (1.7.99).

The class 1.7.3 with oxygen as acceptor is especially preferred here.

Additionally preferred are enzymes of class 1.8, which act on sulfur groups as donors and have as acceptors $NAD^+$, $NADP^+$ (1.8.1), cytochrome (1.8.2), oxygen ($O_2$) (1.8.3), disulfides (1.8.4), quinone (1.8.5), iron-sulfur proteins (1.8.7) or others (1.8.99).

Especially preferred is the class 1.8.3 with oxygen ($O_2$) and (1.8.5) with quinones acceptors.

Additionally preferred are enzymes of class 1.9, which act on heme groups as donors and have as acceptors oxygen ($O_2$), (1.9.3), $NO_2$ compounds (1.9.6) and others (1.9.99).

Especially preferred here is the group 1.9.3 with oxygen ($O_2$) as acceptor (cytochrome oxidases).

Additionally preferred are enzymes of class 1.12, which act on hydrogen as donor.

The acceptors are $NAD^+$ or $NADP^+$ (1.12.1) or others (1.12.99).

Furthermore, enzymes of class 1.13 and 1.14 are preferred (oxygenases).

In addition, preferred enzymes are those of class 1.15, which act on superoxide radicals as acceptors.

Especially preferred here is the superoxide dismutase (1.15.1.1).

Additionally preferred are enzymes of class 1.16.

$NAD^+$ or $NADP^+$ (1.16.1) or oxygen ($O_2$) (1.16.3) act as acceptors.

Especially preferred here are enzymes of class 1.16.3.1 (ferroxidase, for example, ceruloplasmin).

Additionally preferred enzymes are those that belong to group 1.17 (activity on $CH_2$ groups that are oxidized to –CHOH-), 1.18 (activity on reduced ferredoxin as donor), 1.19 (activity on reduced flavodoxin as donor), and 1.97 (other oxoreductases).

Additionally especially preferred are the enzymes of group 31.11, which act on a peroxide as acceptor. This single subclass (1.11.1) contains the peroxidases.

Especially preferred here are cytochrome C peroxidases (1.11.1.5), catalase (1.11.1.6), the peroxydase (1.11.1.6), iodide peroxidases (1.11.1.8), glutathione peroxidase (1.11.1.9), chloride peroxidase (1.11.1.10), L-ascorbate peroxidases (1.11.1.11), phospholipid hydroperoxide glutathione peroxidases (1.11.1.12), manganese peroxidase (1.12.1.13), diarylpropane peroxidase (ligninase, lignin peroxidases) (1.11.1.14).

Really especially preferred are enzymes of class 1.10, which act on biphenols and related compounds. They catalyze the oxidation of biphenols and ascorbates. $NAD^+$, $NADP^+$ (1.10.1), cytochrome (1.10.2), oxygen (1.10.3) or others (1.10.99) act as acceptors.

Of these again enzymes of class 1.10.3 with oxygen ($O_2$) as acceptor are especially preferred.

Of the enzymes of this class the enzymes catechol oxidase (tyrosinase) (1.10.3.1), L-ascorbate oxidase (1.10.3.3), o-aminophenol oxidase (1.10.3.4) and laccase (benzenediol: oxygen oxidoreductase) (1.10.3.2) are preferred, where the laccases (benzenediol: oxygen oxidoreductase) (1.10.3.2) are especially preferred.

The said enzymes are commercially available or can be obtained by standard methods. For example, plants, animal cells, bacteria and fungi are possibilities as organisms for production of the enzymes. Basically both naturally occurring and genetically modified organisms can be enzyme producers. Likewise, parts of one-celled or multicelled organisms are conceivable as enzyme producers, above all cell cultures.

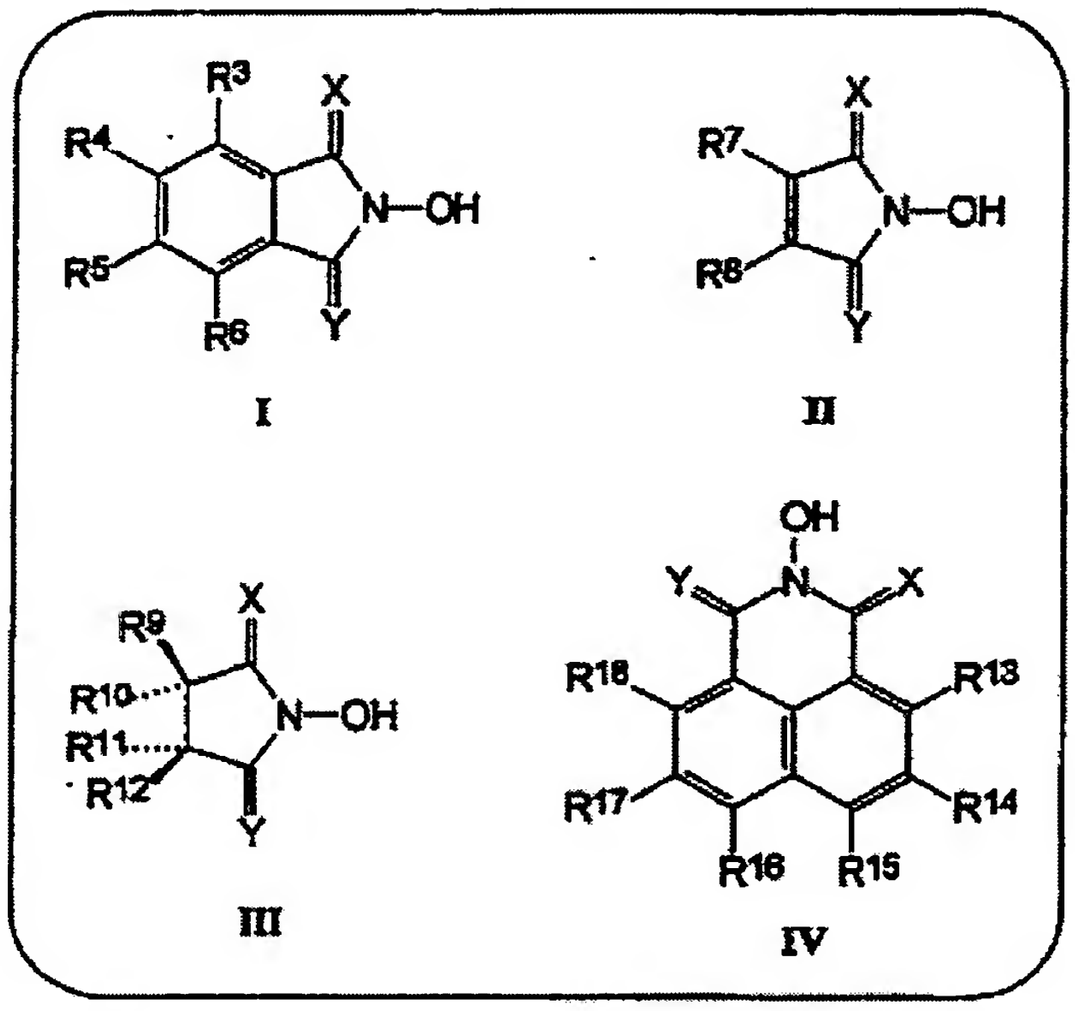
White rot fungi like Pleurotus, Phlebia and Trametes, for example, are used for the especially preferred enzymes such as those from group 1.11.1 above all, but also 1.10.3 and especially for production of liccases.

The multicomponent system in accordance with the invention includes at least one oxidation agent. For example, air, oxygen, ozone, $H_2O_2$, organic peroxides, peracids like peracetic acid, performic acid, persulfuric acid, pernitric acid, metachloroperoxibenzoic acid, perchloric acid, perborates, peracetates, persulfates, peroxides or oxygen species and the radicals

like $OH^*$, $OOH^*$, singlet oxygen, superoxide ($O_2^{*-}$, ozonide, dioxygenyl cation ($O_2^+$), dioxirane, dioxetane or Fremy's radicals can be used as oxidation agents.

Preferably, oxidation agents that can be generated either by the corresponding oxidoreductases, for example, dioxiranes from liccases plus carbonyls, or that can chemically regenerate the mediator or can convert it directly, are preferably used.

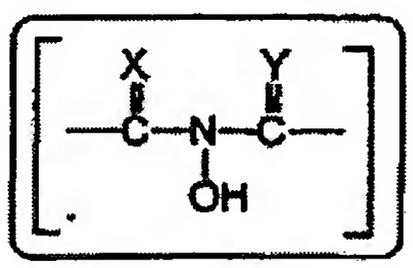
The multicomponent system in accordance with the invention includes, as mediator (component c), preferably at least one compound of the general formulas I, II, III or IV,




where X, Y have the meanings already given, and the residues $R^3$-$R^{18}$ are the same or different and mean a halogen residue, carboxy residue, salt or ester of a carboxy residue or the meanings given for $R^1$, where $R^9$ and $R^{10}$ or $R^{11}$ and $R^{12}$ must not simultaneously mean hydroxy or amino residue, and optionally each two of the components $R^3$-$R^6$, $R^7$-$R^8$, $R^9$-$R^{12}$, $R^{13}$-$R^{18}$, can be bonded to a ring –B-,

where –B- has one of the following meanings:

$(-CH=CH)-_n$ with n 1-3, -CH=CH-CH=N- or




Formula A

and where optionally the residues $R^9$-$R^{12}$ can also be linked to each other via one or two bridge elements -Q-, where -Q- is the same or different and has one of the following meanings: -O-, -S, -$CH_2$-, -$CR^{19} = CR^{20}$-;

where $R^{19}$ and $R^{20}$ are the same or different and have the meaning of $R^3$.

Compounds of the general formulas I, II, III or IV in which X and y mean O or S are especially preferred as mediators.

Examples of such compounds are N-hydroxyphthalimide and optionally substituted N-hydroxyphthalimide derivatives, N-hydroxymaleimide and optionally substituted N-hydroxymaleimide derivatives, N-hydroxynaphthalic acid imide and optionally substituted N-hydroxynaphthalic acid imide derivatives, N-hydroxysuccinimide and optionally substituted N-hydroxysuccinimide derivatives, preferably ones in which the residues $R^9$-$R^{12}$ are polycyclically linked.

N-Hydroxyphthalimide is especially preferred as mediator (component c of the multicomponent system in accordance with the invention.

Compounds of formula I that are suitable as mediator are, for example:

N-hydroxyphthalimide,

N-hydroxybenzene-1,2,4-tricarboxylic acid imide,

N,N'-dihydroxypyromellitic acid diimide,

N,N'-dihydroxybenzophenone-3,3',4,4'-tetracarboxylic acid diimide.

Compounds of formula II that are suitable as mediator are, for example:

N-hydroxyphthalimide,

pyridine-2,3-dicarboxylic acid N-hydroxyimide.

Compounds of formula III that are suitable as mediator are, for example:

N-hydroxysuccinimide,

N-hydroxytartaric acid imide,

N-hydroxy-5-norbornene-2,3-dicarboxylic acid imide,

exo-N-hydroxy-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide,

N-hydroxyciscyclohexane-1,2-dicarboximide,

N-hydroxycis-4-cyclohexene-1,2-dicarboxylic acid imide.

A compound of formula IV that is suitable as mediator is, for example:

N-hydroxynaphthalic acid imide sodium salt.

A compound with a six-member ring containing the structure indicated in formula A that is suitable as mediator is, for example:

N-hydroxyglutarimide.

The compounds indicated as examples are also suitable in the form of their salts or esters as mediators.

The invention also concerns the use of substances that are suitable in accordance with the invention as mediators for modification, decomposition or bleaching of lignin, lignin-containing materials or similar substances. The efficiency of the multicomponent system in modifying, decomposing or bleaching lignin, lignin-containing materials or similar substances is frequency improved even further when, besides the said components, $Mg^{2+}$ ions are also present. The $Mg^{2+}$ ions can be used, for example, as salt, for example, $MgSO_4$. The concentration lies in the range of 0.1-2 mg/g of lignin-containing material, preferably 0.2-0.6 mg/g.

In many cases a further increase of the efficiency of the multicomponent system in accordance with the invention can be achieved if the multicomponent system contains, besides the $Mg^{2+}$ ions, complexing agents such as ethylenediaminetetracetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentamethylenephosphonic acid (DTMPA), nitrilotriacetic acid (NTA), polyphosphoric acid (PPA), etc. The concentration lies in the range of 0.2-5 mg/g lignin-containing material, preferably 1-3 mg.

The use of the multicomponent system in accordance with the invention in a method for treating lignin takes place, for example, by mixing the components a) through c) as in Claim 1 that are selected in each case simultaneously or in any sequence with an aqueous suspension of the lignin-containing material.

Preferably, a method is carried out using the multicomponent system in accordance with the invention in the presence of oxygen or air at normal pressure up to 10 bar and in a pH range from 2-11, at a temperature from 20-95°C, preferably 40-95°C, and a stock consistency of 0.5-40%.

A finding that is surprising and unusual for the use of enzymes in pulp bleaching is that when the multicomponent system in accordance with the invention is used an increase of the stock consistency enables a considerable increase of the kappa number reduction.

For economical reasons a method in accordance with the invention is preferably carried out at stock consistencies from 6-30 wt%, especially preferably 9-15 wt%.

Surprisingly, it also turned out that an acid wash (pH 2-6, preferably 4-5) or Q step (pH 2-6, preferably 4-5) before the enzyme mediator step in many cases leads to a considerable kappa number reduction in comparison to treatment without this particular pretreatment. In the Q step the usual substances for this purpose (for example, EDTA, DTPA) are used as chelate forming agents. They are preferably used in concentrations from 0.1%/t up to 1%/t, especially preferably 0.1%/t to 0.5%/t.

In the method in accordance with the invention preferably 0.01-10,000 units (U) enzyme per g of lignin-containing material is used. Especially preferably 0.1-100, particularly preferably 1-40 U enzyme per g of lignin-containing material is used. (1 U corresponds to the conversion of

1 µmol 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonic acid diammonium salt) (ABTS)/min/mL enzyme).

In the method in accordance with the invention preferably 0.01 mg to 100 mg oxidation agent is used per g of lignin-containing material. Especially preferably, 0.01-50 mg oxidation agent is used per g of lignin-containing material.

In the method in accordance with the invention preferably 0.5-80 mg mediator is used per g of lignin-containing material. Especially preferably, 0.5-40 mg mediator is used per g of lignin-containing material.

Reducing agents can be added at the same time; these serve to establish a specific redox potential together with the oxidation agents that are present.

Sodium bisulfite, sodium dithionite, ascorbic acid, thio compounds, mercapto compounds or glutathione, etc., can be used as reducing agents.

The reaction takes place, for example in the case of laccase with the addition of oxygen or air or oxygen overpressure or air overpressure, while with the peroxidases (for example lignin peroxidases, manganese peroxidases) it takes place with hydrogen peroxide. For example, it is also possible to generate the oxygen in situ through hydrogen peroxide + catalase and hydrogen peroxide can be generated in situ through glucose + glucose peroxidase or other systems.

In addition, radical forming agents or radical scavengers (scavenging of, for example, OH' or OOH' radicals) can also be added to the system. These can improve the interplay within the redox/radical mediators.

It is also possible to add other metal salts to the reaction solution.

These are important in the interaction with chelate-forming agents as radical forming agents or redox centers. The salts form cations in the reaction solution. Such ions are, among others, $Fe^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Mn^{3+}$, $Mn^{4+}$, $Cu^{2+}$, $Ca^{2+}$, $Ti^{3+}$, $Cer^{4+}$, $Al^{3+}$.

Moreover, the chelates present in the solution can serve as mimic substances for the enzymes, for example for the laccases (copper complexes) or for the lignin or manganese peroxidases (heme complexes). Mimic substances are understood to be substances that (here) can simulate the prosthetic groups of oxidoreductases and can, for example, catalyze oxidation reactions.

In addition, NaOCl can be added to the reaction mixture.

This compound can form singlet oxygen in the interaction with hydrogen peroxide.

Finally, it is also possible to operate while using detergents. Possibilities as such are nonionic, anionic, cationic and amphoteric surfactants. The detergents can improve the penetration of the enzymes and mediators and to the fibers.

In the same way, it can be necessary for the reaction to add polysaccharides and/or proteins. Here one should mention in particular as polysaccharides glucans, mannans, dextrans,

levans, pectins, alginates or vegetable gums and/or characteristic polysaccharides produced by the fungi or produced in the mixed culture with yeasts, and one may mention as proteins gelatins and albumin. These substances mainly serve as protective colloids for the enzymes.

Other proteins that can be added are proteases like pepsin, bromelin, papain, etc. These can serve, among other things, to yield better access to the lignin through the decomposition of the extensin C, a hydroxyproline-rich protein, that is present in the wood.

Possibilities as other protective colloids are amino acids, simple sugars, oligo sugars, PEG types of various molecular weights, polyethylene oxides, polyethyleneimines, and polydimethylsiloxanes.

The method in accordance with the invention cannot only be used in the delignification (bleaching) of sulfate, sulfite, organosol, etc., celluloses and pulps, but also in the production of celluloses or pulps (refinery pulp/wood pulp) generally, for example, from wood or annual plants. For this a defibrization via the usual cooking processes and/or mechanical processes or pressure (i.e., a very mild treatment up to kappa numbers in the range of >50 kappa or >10% lignin) should be guaranteed.

In the bleaching of celluloses, as in the production of celluloses, the treatment can be repeated several times, either after washing and extracting the treated substance with NaOH or without this intermediate step. This leads to still more reduced kappa values and to considerable increases of whiteness. In the same way an $O_2$ step can be used before the enzyme/mediator treatment or, as already noted, an acid wash or Q step (chelate step) can also be carried out.

Below the invention is illustrated in more detail by means of examples:

Example 1

Enzymic bleaching with N-hydroxyphthalimide and softwood sulfate pulp

5 g bone dry pulp (softwood $O_2$, delignified), stock consistency 30% (about 17 g wet) is added to the following solutions:

A) 20 mL tap water is mixed with 30 mg N-hydroxyphthalimide (HPI) while stirring, the pH is adjusted with 0.5 mol/L $H_2SO_4$ solution so that after adding the pulp and the enzyme a pH of 4.5 results.

B) 5 mL tap water is mixed with the amount of laccase from *Trametes versicolor* so that an activity of 35 U (1 U = conversion of 1 µmol ABTS/min/mL of enzyme) per g of pulp results.

Solutions A and B are added together and brought up to 33 mL.

After adding the pulp mixing with a dough kneader is carried out for 2 min.

Then the pulp is put into a reaction bomb preheated to 45°C and incubated for 1-4 h under 1-10 bar oxygen over pressure.

Then the substance is washed through a nylon sieve (30 μm) and extracted for 1 h at 60°C, 2% stock consistency and 8% NaOH per g of pulp (bone dry).

After rewashing the pulp the kappa number is determined. The result is given in Table 1.

Example 2

Enzymic bleaching with N-hydroxyphthalimide and hardwood sulfate pulp

55 g [sic] bone dry pulp (hardwood $O_2$, delignified), stock consistency 30% (about 17 g wet) is added to the following solutions:

A) 20 mL tap water is mixed with 30 mg N-hydroxyphthalimide (HPI) while stirring, the pH is adjusted with 0.5 mol/L $H_2SO_4$ solution so that after adding the pulp and the enzyme a pH of 4.5 results.

B) 5 mL tap water is mixed with the amount of laccase from *Trametes versicolor* so that an activity of 35 U (1 U = conversion of 1 μmol ABTS/min/mL of enzyme) per g of pulp results.

Solutions A and B are added together and brought up to 33 mL.

After adding the pulp, mixing with a dough kneader is carried out for 2 min.

Then the pulp is put into a reaction bomb preheated to 45°C and incubated for 1-4 h under 1-10 bar oxygen over pressure.

Then the substance is washed through a nylon sieve (30 μm) and extracted for 1 h at 60°C, 2% stock consistency and 8% NaOH per g of pulp (bone dry).

After rewashing the pulp the kappa number is determined. The result is given in Table 1.

Example 3

Enzymic bleaching with N-hydroxymaleimide and softwood sulfate pulp

5 g bone dry pulp (softwood $O_2$, delignified), stock consistency 30% (about 17 g wet) is added to the following solutions:

A) 20 mL tap water is mixed with 30 mg N-hydroxymaleimide (HPI) while stirring, the pH is adjusted with 0.5 mol/L $H_2SO_4$ solution so that after adding the pulp and the enzyme a pH of 4.5 results.

B) 5 mL tap water is mixed with the amount of laccase from *Trametes versicolor* so that an activity of 35 U (1 U = conversion of 1 μmol ABTS/min/mL of enzyme) per g of pulp results.

Solutions A and B are added together and brought up to 33 mL.

After adding the pulp mixing with a dough kneader is carried out for 2 min.

Then the pulp is put into a reaction bomb preheated to 45°C and incubated for 1-4 h under 1-10 bar oxygen over pressure.

Then the substance is washed through a nylon sieve (30 μm) and extracted for 1 h at 60°C, 2% stock consistency and 8% NaOH per g of pulp (bone dry).

After rewashing the pulp the kappa number is determined. The result is given in Table 1.

Table 1. Results of Examples 1-3

| System | Kappa before extraction | Kappa after extraction | Lignin decomposition (%) |
|---|---|---|---|
| Control value Softwood $O_2$ | 9.6 | 9.3 | 3.1 |
| HPI + Softwood $O_2$ | 7.8 | 6.7. | 30.2 |
| Control value Hardood | 12.7 | 11.5 | 9.5 |
| HPI + Hardwood | 10.8 | 9.4 | 26 |
| Control value Softwood $O_2$ | 9.6 | 9.3 | 3.1 |
| N-Hydroxymaleimide + Softwood $O_2$ | 9.1 | 8.1 | 15.6 |

The results refer to an incubation time of 4 h.

Example 4

Hydrolysis of N-hydroxyphthalimide in water (characteristic decomposition of mediator)

30 g N-Hydroxyphthalimide (HPI) is dissolved in 50 mL tap water in a reaction vessel and adjusted to pH 4.5 with 0.5 mol/L $H_2SO_4$ solution, This solution is stirred for 5 h at a temperature of 45°C.

After the given incubation time the HPI has converted 30% to phthalic acid and hydroxylamine. Here the phthalic acid and hydroxylamine result in equal molar parts.

Claims

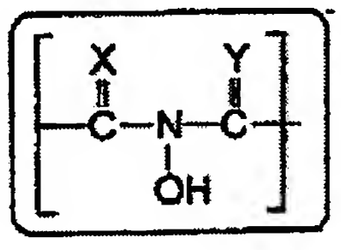
1. A multicomponent system for modification, decomposition or bleaching of lignin, lignin-containing materials, or similar substances, containing

a. optionally at least one oxidation catalyst and

b. at least one suitable oxidation agent and

c. at least one mediator,

which is characterized by the fact that the mediator is chosen from the group of cyclic N-hydroxy compounds with at least one, optionally substituted, five- or six-member ring containing the structure indicated in formula A




Formula A

and its salts, ethers or esters, where

X and Y are the same or different, and mean O, S or $NR^1$, where

$R^1$ means hydrogen, hydroxy, formyl, carbamoyl, sulfono residue, ester or salt of the sulfono residue, sulfamoyl, nitro, amino, phenyl, aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl, phospho, phosphono, phosphonooxy residue, esters or salts of the phosphonooxy residue, where carbamoyl, sulfamoyl, amino and phenyl residues can be unsubstituted or substituted one or more times with a residue $R^2$, and the aryl $C_1$-$C_5$ alkyl, $C_1$-$C_{12}$ alkyl, $C_1$-$C_5$ alkoxy, $C_1$-$C_{10}$ carbonyl, carbonyl $C_1$-$C_6$ alkyl residues can be saturated or unsaturated, branched or unbranched, and can be substituted one or more times with a residue $R^2$, where,

$R^2$ is the same or different and means hydroxy, formyl, carboxy, ester or salt of the carboxy residue, carbamoyl, sulfono ester or salt of the sulfono residue, sulfamoyl, nitro, amino, phenyl, $C_1$-$C_5$ alkyl, $C_1$-$C_5$ alkoxy residue.

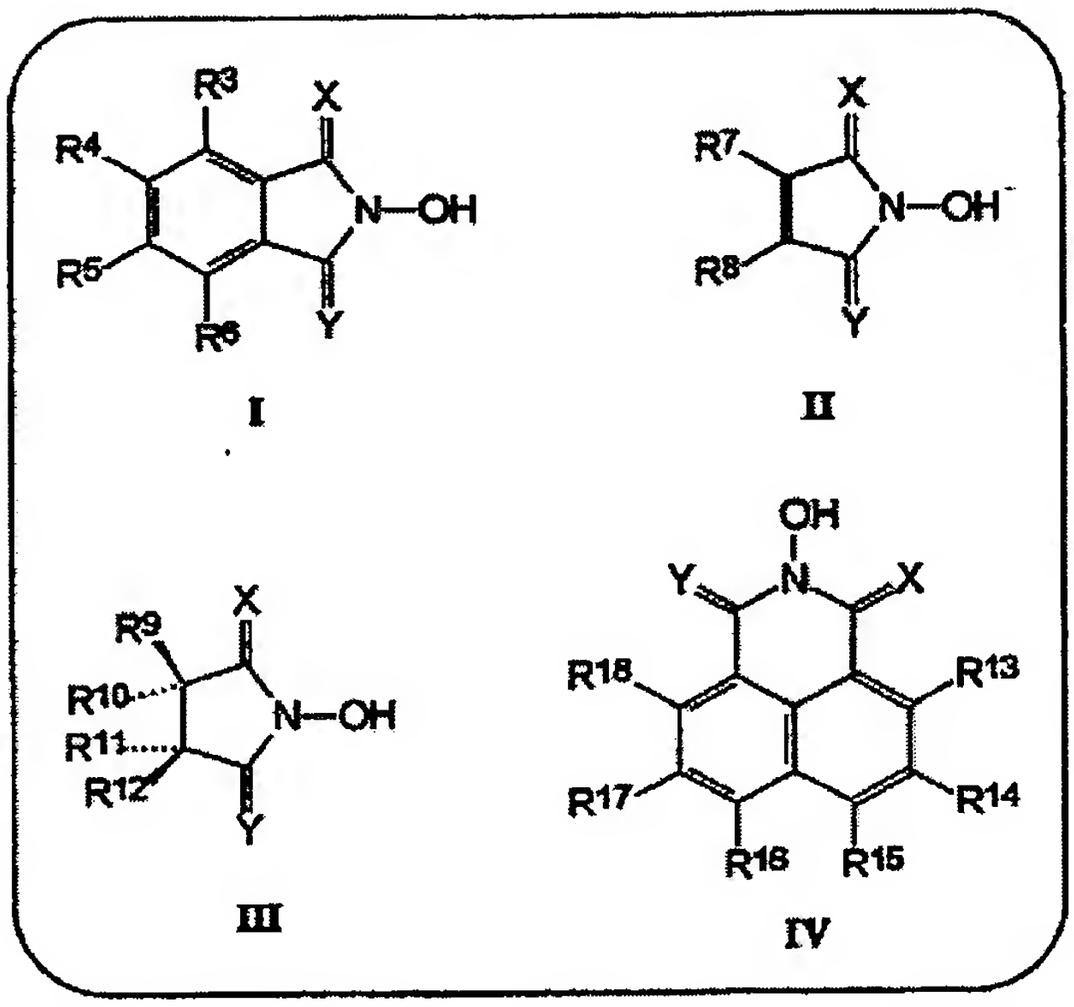
2. A multicomponent system as in Claim 1, which is characterized by the fact that it includes at least one oxidation catalyst.

3. A multicomponent system as in Claim 1 or 2, which is characterized by the fact that an enzyme is used as oxidation catalyst.

4. A multicomponent system as in one of Claims 1-3, which is characterized by the fact that laccase is used as enzyme.

5. A multicomponent system as in one of Claims 1-4, which is characterized by the fact that air, oxygen, ozone, $H_2O_2$, organic peroxides, peracids like peracetic acid, performic acid, persulfuric acid, pernitric acid, metachloroperoxibenzoic acid, perchloric acid, perborates, peracetates, persulfates, peroxides or oxygen species and their radicals like $OH^*$, $OOH^*$, singlet oxygen, superoxide ($O_2^{*-}$), ozonide, dioxygenyl cation ($O_2^+$), dioxiranes, dioxetanes or Fremy's radicals are used as oxidation agents.

6. A multicomponent system as in one of Claims 1-5, which is characterized by the fact that at least one compound of the general formulas I, II, III or IV,

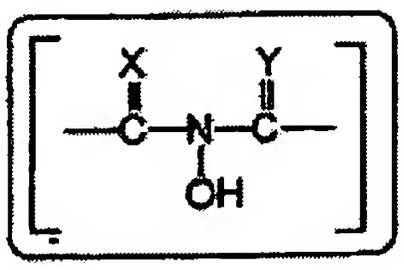



where X and Y have the meanings that were already given and the residues $R^3$-$R^{18}$ are the same or different and mean halogen residue, carboxy residue, salt or ester of a carboxy residue or have the meaning given for $R^1$,

where $R^9$ and $R^{10}$ or $R^{11}$ and $R^{12}$ must not simultaneously mean hydroxy or amino residue and

optionally each two of the components $R^3$-$R^6$, $R^7$-$R^8$, $R^9$-$R^{12}$, $R^{13}$-$R^{18}$ can be linked to a ring -B-, where -B- has one of the following meanings:

$(-CH=CH)-_n$ with n 1-3, -CH=CH-CH=N- or



Formula A

and where optionally the residues $R^9$-$R^{12}$ can also be linked to each other via one or two bridge elements -Q-, where –Q- can be the same or different and can have the following meanings:

-O-, -S, $-CH_2-$, $-CR^{19} = CR^{20}-$;

where $R^{19}$ and $R^{20}$ are the same or different and have the meaning of $R^3$,

is used as mediator component (component c).

7. A multicomponent system as in one of Claims 1-6, which is characterized by the fact that at least one substance chosen from the group N-hydroxyphthalimide, optionally substituted

N-hydroxyphthalimide derivatives, N-hydroxymaleimide, optionally substituted N-hydroxymaleimide derivatives, N-hydroxynaphthalic acid imide, optionally substituted N-hydoxynaphthalic acid imide derivatives, N-hydroxysuccinimide, optionally substituted N-hydroxysuccinimide derivatives, are used as mediator.

8. A multicomponent system as in one of Claims 1-6, which is characterized by the fact that N-hydroxyphthalimide is used as mediator.

9. A method for treating lignin, which is characterized by the fact that the components (a) through (c) as in Claim 1 that are chosen in each case are mixed simultaneously or in any sequence with an aqueous suspension of the lignin-containing material.

10. The use of mediators as in Claim 1 for modification, decomposition or bleaching of lignin, lignin-containing materials, or similar substances.